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Green's functional analysis of polarisation in mixed KDP-DKDP system

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This is a sequel of our earlier work on ferroelectric polarization in KDP(KH_2PO_4) with pure tunneling mode Here a theoretical discussion has been made about the nature of dielectric polarization in a mixed KDP-DKDP (DKDP = KD_2PO_4) crystal using double time temperature dependent Green's functional analysis Effect of coupled proton-lattice mode has also been discussed.

After the pioneering work in this line by Slater (1941), a model similar to Ising model in a transverse field was first proposed by De-Gennes (1963) to study the ferroelectric properties of KH_2PO_4 In KDP there are two positions of minimum potential energy in a hydrogen bond (O - **H** ..O bond), one near each oxygen, and the proton can tunnel through the barrier which separates them The ground state then splits into two levels, separated by the tunneling energy 2Ω. De-Gennes (1963) and Nettleton (1967) regarded this two level system as a pseudo-spin S system. Assuming some direct interaction between protons one can write a pseudo-spin Hamiltonian valid for a pure KDP of the form (Konwent 1968, Tokunaga & Matsubara 1966)

$$H = -2\sum_i S_i^x \Omega_i - \sum_i \mu_i S_i^z E - \tfrac{1}{2}\sum_{ij} S_i^z S_j^z I_{ij} \qquad (1)$$

where E is the electric field along the Z-direction—the C-axis of the crystal, μ_i is the dipole moment along O - H. .O bond, $S_i^\alpha (\alpha = x,y,z)$ is the α-component of the pseudo-spin, ij label the proton sites and I_{ij} is the proton-proton interaction

In the mixed system the interaction not only depends on the position of the bond but also on the nature of the bond (whether D or H) Considering dipole-dipole character of the interaction the Hamiltonian (1) can be re-written in the form (Holakovsky 1972)

$$H_A = -2[\Omega_A S_i^x + S_i^z \mu_A (E + 2\mu_D \sum_{j\in D} S_j^z J_{ij} + 2\mu_H \sum_{j\in H} S_j^z J_{ij})] \qquad (2)$$

where the i-th bond is occupied by a A type atom ($A = H$ or D)

Let us define thermodynamic Green's function like

$$G^{mn}(i,j;t) = -i\theta(t-t')\langle[S_i^m(t), S_j^n(t')]\rangle \quad .. \quad (3)$$

where $(m, n) = x, y, z$ and $\theta(t-t')$ is the step-function. The Fourier transform of the Green's function (GF) follow equation like

$$E \ll S_i^m(t); S_j^n(t') \gg_E = (2\pi)^{-1}\langle[S_i^m(t), S_j^n(t')]_-\rangle + \ll [S_i^m(t), H_A]_-; S_j^n(t') \gg_E \quad ... \quad (4)$$

The solution of eq. (4) for $G^{mn}(i,j,E) = \ll S_i^m(t); S_j^n(t') \gg_E$ in conjunction with the spectral theorem (Zubarev 1960) gives the following thermal average (for decoupling the complex GF we adopt the procedure of Bogoliubov & Tyablikov 1959; for details see Chaudhuri 1976a 1976b)

$$\langle S_A^z \rangle = -\frac{\theta S(S+1)}{[\theta^2+\phi^2]^{\frac{1}{2}}} \tanh \beta/2[\theta^2+\phi^2]^{\frac{1}{2}} \quad ... \quad (5)$$

where $\theta = 2[\mu_A E + 2(N_D\mu_D + N_H\mu_H)\mu_A J' \langle S_A^z \rangle$, $J' = \sum_j J_{ij}$, $\phi = 2\Omega$ and J_{ij} is the proton–proton interaction of the mixed system (J' is the Fourier transform of J_{ij}) N_H and N_D are the concentrations of H and D atoms $\beta = 1/k_B T$, k_B and T being respectively the Boltzmann constant and the absolute temperature

In absence of electric field $E = 0$, there is a solution of eq (5) viz. $\langle S_A^z \rangle = 0$ The critical temperature T_C in the limit $\langle S_A^z \rangle \to 0$ is given by

$$\frac{\Omega_A}{\bar{m}J'} = 2\mu_A S(S+1) \tanh \frac{\Omega_A}{k_B T_C} \quad .. \quad (6)$$

where $\bar{m} = (N_H\mu_H + N_D\lambda_D)$ The other solution of $\langle S_A^z \rangle$ (eq 5) gives the spontaneous polarization at any temperature

$$P = 2\bar{m}\langle S_A^z \rangle \quad .. \quad (7)$$

The equation for $\langle S_A^z \rangle$ should be solved self-consistently as has been done in our earlier work Chaudhuri (1976). In the para-electric (PE) phase $\langle S_A^z \rangle = 0$ and hence $P = 0$ At $T \ll T_C$ the spins are not completely aligned because of finite tunneling probability even at $T = 0$ At $T \ll T_C$, there occurs a saturation in polarization given by

$$P_S = \bar{m}(1 - 16\Omega_A^2/m'J')^{\frac{1}{2}}. \quad ... \quad (8)$$

where $m' = (N_H + N_D)$

The tunneling model also yields an expression for the temperature dependent dielectric constant $\epsilon(T)$ in the para-electric phase (Blinc & Zeks 1972)

$$\epsilon(T) = \epsilon_l + \frac{4(\mu_H^2 N_H + \mu_D^2 N_D)\tanh(\Omega_A/k_B T)}{4\Omega_A - m' J' \tanh(\Omega_A/k_B T)} \quad \ldots (9)$$

where ϵ_l is the lattice dielectric constant and the second term represents the soft-mode contribution to $\epsilon(T)$. About T_C, $\epsilon(T)$ follows a Curie-Weiss law similar to the pure system (Chaudhuri & Saha 1976b)

$$\epsilon(T) \sim C/T - T_C. \quad \ldots (10)$$

where C is the Curie constant given by

$$C = 16(\mu_H^2 N_H + \mu_D^2 N_D) k_B T_C^2/(m'^2 J'^2 - 16\Omega_A^2) \quad \ldots (11)$$

So far we have not considered the coupling between the proton motion and optic modes of the lattice. It can be shown that in the coupled proton-optic mode model (Kobayashi 1968) eq. (6) is modified as

$$\frac{4\Omega_A}{m J^*} = S(S+1)\tanh \Omega_A/kT^*_B, \quad \ldots (12)$$

where $J^* = J' + 4|G_i|^2/\omega_j^2 = J' + 4G^*$; $|G|^2$ is the proton-lattice interaction, ω_j is the frequency of the optic mode and T^* is the temperature at which soft mode vanishes (the transition temperature). The expression for polarization will also be similarly modified in the coupled mode model. It is evident that the coupled mode model J' is increased by $4G^*$ and pure tunneling model is thus a special case of coupled mode model.

The above calculation for a mixed KDP-DKDP system indicates that Curie temperature and dielectric polarization are functions of concentrations of D and H atoms in the mixed system. Using Landau theory of continuous phase transition (Landau 1965) it can also be shown (Chaudhuri & Saha 1976b) that in this system the nature of phase transition not only depends on the ratio Ω/J' (like pure system) but is also governed by the relative concentrations of H and D. Thus the D-atom (or H atom) in pure KDP system (or in pure DKDP system) just behaves as impurity in a pure crystal. More about the nature of phase transition in a mixed KDP–DKDP system along with detailed calculations will appear soon.

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References

Blinc R. & Zeks B. 1972 *Adv. Phys* **21**, 693.
Bogolyubov N. N. & Tyablikov S. V. 1959 *Soviet Phys Dokl.* **4**, 604.
Chaudhuri B. K. 1976a *Indian J. Pure & Appl. Phys.* **14**, 525
Chaudhuri B. K. & Saha M. 1976b, *Phys. Rev. Lett.* (in press)
De-Gennes P. G. 1963 *Solid St. Commun.* **1**, 132
Holakovsky J. 1972 *Czech. J. Phys.* **B22**, 651
Konn, 1968 *Phys St Solidi* **28**, 39.
Landau D. L 1965 *Collected papers of Landau*, Edited by D. ter Haar, Pergamon Press (pp 193–266).
Nettleton R. E. 1967 *Phys. St Solidi* **24**, 561.
Slator J. C. 1951 *J. Chem Phys.* **9**. 16
Tokunaga M. & Matsubara T. 1966 *Prog. Theo. Phys.* **35**, 581.